

COMBUSTION PROPERTIES OF COAL-CHAR BLENDS: NO_x EMISSION CHARACTERISTICS

Massoud Rostam-Abadi¹, Latif Khan¹, Joseph A. DeBarr¹
L. D. Smoot², G. J. Germane², and C. N. Eatough²

¹Illinois State Geological Survey, Champaign, IL 61820

²Advanced Combustion Engineering Research Center
Brigham Young University, Provo, UT 84602

Key words: Combustion, NO_x Reduction, Coal-Char Blend

INTRODUCTION

Nitric oxide formation in hydrocarbon flames occurs primarily through three mechanisms; thermal NO (the fixation of molecular nitrogen by oxygen atoms produced at high temperatures), fuel NO (the oxidation of nitrogen contained in the fuel during combustion), and prompt NO (the attack of a hydrocarbon radical on molecular nitrogen). Of these three mechanisms, fuel NO is by far the most significant source of NO in practical coal flames [1].

It has been suggested that NO_x produced early in pulverized coal flames is subsequently reduced to N₂ by char/NO_x interactions [1]. NO_x can be both produced and reduced by heterogeneous char reactions. For some cases, as much as half of the fuel nitrogen remains in the coal after devolatilization [2]. The amount retained apparently is a function of the reactor stoichiometry [3]. Heterogeneous NO_x often accounts for 20-30 percent of the total NO_x formed [4, 5, 6]. The exact amount appears to be dependent on the temperature and extent of devolatilization. The rate of heterogeneous NO_x reduction has been investigated by many researchers [1, 7, 8, 9]. Essentially, char reduction of NO_x begins only after oxygen is locally depleted in the reactor [10]. The heterogeneous destruction reactions have been determined to be significant in fuel-lean conditions for char combustion, but for fuel-rich coal combustion, the reduction reactions in the gaseous phase appears to control reaction rate [11]. CO enhances NO_x reduction due to surface catalysis of the NO/CO reaction [1, 7]. In the absence of CO, the char-NO_x reduction rate is controlled by the dual-site mechanism of absorbed NO_x [12]. In the presence of CO, the controlling step is the reaction of gaseous NO_x and absorbed NO_x at an active site to form N₂, CO₂, and an oxide complex. Water and O₂ were reported to inhibit the reaction due to the buildup of a chemisorbed layer of oxygen on the char surface [1,12].

The primary goal of this study was to investigate the concept of lowering NO_x emissions by co-firing pulverized Illinois coal with char in a practical flame. A summary of the results obtained is presented in this paper.

EXPERIMENTAL

Coal-Char Blends - A continuous feed charring reactor was used for producing char samples from an Illinois No. 6 coal (38% volatile matter, dry basis). Char samples were pulverized to 70% minus 200 mesh. Pulverized coal (70% minus 200 mesh) was mixed with either the char or powder activated carbon (Calgon Carbon Company) to prepare the following blends:

- Blend 1: 125 pounds of 12.5% char - 87.5% coal
- Blend 2: 500 pounds of 25% char - 75% coal
- Blend 3: 125 pounds of 50% char - 50% coal
- Blend 4: 125 pounds of 12.5% activated carbon-87.5% coal

Proximate and ultimate analyses of the fuels and pore area and pore volume of the coal, char, and activated carbon were determined.

Combustion Tests - Combustion tests were performed with the coal and blends in a 0.5-1.0 Mbtu/hr combustor located at Brigham Young University (BYU) Advanced Combustion Engineering Research Center (ACERC). The combustor, referred to as a controlled profile reactor (CPR), is a cylindrical, down-fired reactor with an inside diameter of 0.80 m and a length of 2.40 m [13]. The burner consists of a central fuel injection tube surrounded by a swirling annular jet of secondary air. The secondary air is preheated to about 500 F and passes through a moveable-block swirl generator capable of varying secondary swirl number from 0 to 5.

Thirteen combustion tests were performed. The first three test were to establish base combustion conditions of the coal only, with no char addition. Tests 4 and 5 were performed to investigate the in situ capture of SO₂ by a high surface area hydrated lime. The remaining tests were designed to determine the ability to reduce NO_x by the coal-char blends. In all combustion tests, effluent gas and solid samples were collected and analyzed.

RESULTS AND DISCUSSION

Properties of Coal-Char Blends- Table 1 compares the proximate analyses of the coal, char (mixture of all char samples ground to -200 mesh), and the blends. The volatile matter (VM) and H-T ash contents of the char were 16.2 and 16.7 wt% (dry basis) compared to 38 and 12.4 wt% for the coal. The VM contents of the blends ranged from 27.3 wt% for the coal-activated carbon blend to 35.6 wt% for the 12.5% char - 87.5% coal blend. As summarized in Table 2, sulfur and nitrogen contents and Btu/lb values of the coal and blends were comparable (3.17 to 3.41% S; 1.20 to 1.33% N; and 12,047 to 12,182 Btu/lb).

The nitrogen-BET pore area of the char was $15.7 \text{ m}^2/\text{g}$ compared to $1012 \text{ m}^2/\text{g}$ for the powder activated carbon, Table 3. The pore area of the coal was $18.8 \text{ m}^2/\text{g}$ indicating that during charring some of the macropores were blocked or destroyed. Nevertheless, char should have micropore area of about 100-400 m^2/g . Micropore area is measured by CO_2 adsorption which was not performed in this study.

Combustibility of Coal-Char Blends- The combustion test matrix is shown in Table 4. Flame temperatures were recorded for the base test condition noted as test 1 and for tests 8-10, 12 and 13. An axial temperature profile was made during test 1. Peak centerline flame temperature was recorded at the 28 cm axial location. Therefore, subsequent characteristic centerline flame temperatures were measured during tests 8-10 and 12, 13 at the 28 cm axial location. The flame temperature measurements are shown in Figure 1.

The effect of char addition to the coal on carbon burnout is shown graphically in Figure 2. Carbon burnout increased with initial increase in percent char in the fuel and decreased slightly with additional char. Visually the flame was stable but became more detached from the burner and flickered at the highest char percentage. Volatile content of the fuel is important to flame stability and therefore burnout. By increasing the char content, the volatile content is decreased resulting in greater flame instability.

Figure 3 shows the measured increase in effluent NO_x concentrations with increasing combustion temperature for the combustion tests performed for this study. Effluent NO_x concentrations in combustion systems is known to increase with combustion temperature [14, 15] due mainly to the increase in thermal NO_x production.

Figure 4 shows the effect that increasing stoichiometry has on effluent NO_x values. Since conversion of fuel nitrogen to NO depends on the availability of oxygen atoms, an increase in effluent NO_x values with increasing stoichiometric ratio was expected. The reason for the stronger dependence noticed for the 0% compared with the 25% char case deserves further investigation.

In order to determine the effect of NO_x reduction on char surfaces during combustion, other NO_x producing or reducing factors must be accounted for. For example, if NO_x is noticed to decrease with increasing char in the fuel, is the effect due to the addition of more NO_x reduction sites on the char surfaces, or from the decrease in burnout and therefore release of fuel nitrogen, or from the decrease in flame temperature and subsequent decrease in the production of thermal NO_x . In coal combustion, fuel nitrogen is certainly the dominant source of NO_x [16]. Since it has been shown that fuel nitrogen evolves from coal particles at approximately the same rate as carbon is consumed [16, 17], the fuel nitrogen release and therefore production of fuel NO_x can be corrected for burnout. Thermal NO_x contributions can be subtracted from total NO_x if the temperature dependence is known. Previous natural gas combustion tests performed using the CPR provided thermal NO_x concentrations as a function of flame temperature [8]. This correlation indicates that only about 10% of the effluent NO_x values measured during these combustion tests originated as thermal NO_x .

Figure 5 shows the effect of increasing percentage of char in the fuel on effluent NO_x concentrations. In order to reduce other NO_x producing and reducing effects as much as possible, these NO_x values have been corrected for burnout as well as thermal NO_x . The trends show a slight initial increase in NO_x with addition of char in the fuel but subsequently NO_x decreases with additional char.

NO_x levels are shown to increase with addition of small amounts of char to the fuel stream. However, an almost linear reduction in NO_x values is noted with increasing char above 12.5%. The reason for the initial increase in NO_x values is not well understood. It is likely that the addition of char extends the reaction zone allowing for greater mixing of fuel and combustion air so that a greater percentage of fuel nitrogen is released in a more oxygen rich environment causing amine radicals to oxidize to NO rather than molecular nitrogen. This explanation is substantiated by the observation that the 12.5% activated carbon-coal blend produced slightly higher effluent NO_x levels than the 12.5% char-coal blend. The low volatile content of activated carbon, and hence, low reactivity, would cause it to lengthen the reaction zone to a greater extent than the addition of 15% volatile content char.

Establishing additional carbon sites by blending char with the coal in the feed stream, along with increasing the NO-carbon contact time, may enhance the effectiveness of the NO reactions. This may account for the measured decrease in NO with additional char. Additional near burner testing or modeling of the combustion system may provide insight into this phenomenon.

SUMMARY AND RECOMMENDATIONS

Blending char with parent coal may have some merit as a viable NO_x reduction scheme for high values of char addition (ie, above 40%). It is recommended that future work be aimed at using high surface area char and increasing the stability of high char content fuels by studying the effect of parameters such as air preheat, burner geometry, and gas or oil assist. The effect of different types of char and injection location (temperature) on the effluent NO_x concentration should also be investigated.

The increase in effluent NO_x concentration with low levels of char blended with coal is not well understood. It is recommended that fuel nitrogen partitioning studies be performed to determine the separate relationships between volatile and char nitrogen on effluent NO_x . It is also recommended that near burner combustion tests be performed to study the fate of NO_x precursors in coal and coal-char flames.

ACKNOWLEDGMENTS

This work was sponsored by the Illinois Department of Energy and Natural Resources through the Illinois Coal Development Board and Illinois Clean Coal Institute, and the United State Department of Energy.

REFERENCES

1. Levy, J. M., L. K. Chan, F. Sarofim, and J. M. Beer, "NO/Char Reactions at Pulverized Coal Flame Conditions," 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 111 (1981).
2. Pershing, D. W. and J.O.L. Wendt, "Relative Contributions of Volatile Nitrogen and Char Nitrogen to NO_x Emissions from Pulverized Coal Flames," Ind. Eng. Chem. Process Des. Dev., 18,1 (1979).
3. Glass, J. W., and J.O.L. Wendt, "Mechanisms Governing the Destruction of Nitrogenous Species During the Fuel Rich Combustion of Pulverized Coal," 19th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, p. 1243 (1982).
4. Pohl, J. H., and A. F. Sarofim, "Fate of Coal Nitrogen During Pyrolysis and Oxidation," EPA Symposium on Stationary Source Combustion, Atlanta, GA, (September, 1975); Proceedings of the Stationary Source Combustion Symposium, I, EPA 600/2-76-152a, June (1976).
5. Heap, M. P., T. M. Lowes, R. Walmsley, H. Bartelds, and P. LeVaguerese, "Burner Criteria from NO_x Control: Influence of Burner Variables on NO_x in Pulverized Coal Flames," U.S.E.F.T.S., EPA-600/2-76-061a (1976).
6. Pershing, D. W., and J. O. L. Wendt, 1977. "Pulverized Coal Combustion: The Influence of Flame Temperature and Coal Composition on Thermal and Fuel NO_x ," Paper presented at the 16th International Symposium on Combustion, p. 389, Pittsburgh, PA.
7. Sheref, M and K. Otto, "Simultaneous Catalytic Reaction of O_2 and NO with CO and Solid Carbon", Jrn of Coll. and Interface Science, 31:1,73 (1969).
8. Song, Y.H., D.W. Blair, V.J. Siminski, and W. Bartok, "Conversion of Fixed Nitrogen to N_2 in Rich Combustion," Eighteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 53 (1981).
9. Glass, J. W., and J.O.L. Wendt, "Mechanisms Governing the Destruction of Nitrogenous Species During the Fuel Rich Combustion of Pulverized Coal," Western States Section/Combustion Institute, University of Utah, Salt Lake City, UT (1982).
10. Wendt, J.O.L., D. W. Pershing, J. W. Lee, and J. W. Glass, "Pulverized Coal Combustion: NO_x Formation Mechanisms Under Fuel Rich and Staged Combustion Conditions," 17th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, p.77 (1979).
11. Glass, J.W. and J.O.L. Wendt, "Advanced Staged Combustion Configurations for Pulverized Coal: Fuel Nitrogen Conversion During Fuel Rich Combustion of Pulverized Coal and Char," U.S. Department of Energy Topical Report No. 1, DOE/ET-75184-1152 (1981).
12. Sheppard, W.M., "A Kinetic Study of the Reaction of Nitric Oxide and Active Carbon," Doctoral Dissertation, Clemson University.
13. Eatough, C.N., Controlled Profile Reactor Design and Combustion Measurements, Ph.D. Dissertation, Department of Mechanical Engineering, Brigham Young University, Provo, UT, 1991.
14. Boardman, R.D., C.N. Eatough, G.J. Germane, and L.D. Smoot, "Comparison of Measurements and Predictions of Flame Structure and Thermal NO_x in a Swirling, Natural Gas Diffusion Flame," Combustion Science and Technology, vol. 93, 1993, pp. 193-210.
15. Zel'dovich, Y.B., P.Y. Sadovnikov, and D.A. Frank-Kamenskii, "Oxidation of Nitrogen in Combustion," (translated by Sheref), Academy of Sciences of USSR, 1947.
16. Smoot, L.D., (Editor), Fundamentals of Coal Combustion for Clean and Efficient Use, Elsevier, New York, NY, 1993.
17. Chen, J.C., and S. Niksa, "Suppressed Nitrogen Evolution From Coal-Derived Soot and Low-Volatility Coal Chars," 24th Symposium, International, on Combustion, The Combustion Institute, Pittsburgh, PA, 1992, pp. 1269-1276.

Table 1. Proximate analyses of fuels (wt %, dry basis)

	Coal	Blend 1	Blend 2	Blend 3	Blend 4	Char
moisture	12.5	10.4	8.8	6.4	11.7	2.11
volatile matter	38.0	35.6	32.9	27.3	34.7	16.2
fixed carbon	49.6	51.3	53.7	58.3	54.2	67.1
H-T ash	12.4	13.2	13.4	14.4	11.1	16.7

* minus 200 mesh samples

Table 2. Analysis of fuels (wt%, dry basis)

	Coal	Char	Blend 1	Blend 2	Blend 3	Blend 4
Nitrogen	1.33	1.46	1.30	1.34	1.42	1.29
Sulfur	3.41	2.83	3.31	3.27	3.09	3.17
Btu/lb	12,182		12,138	12,169	12,047	12,480

Table 3. Pore area and pore volume data

	Coal	Char	Activated Carbon
Pore area (m ² /g)	18.8	15.71	1012
Pore volume (cc/g)	0.0342	0.145	

Table 4. Combustion Test Matrix.

Test No.	Description	Fuel Feed Rate (kg/hr)	Air Feed Rate (kg/hr)	Stoichiometric Ratio ¹
1	Coal	11.4	96.4	1.08
2	Coal	11.4	110.0	1.24
3	Coal	11.4	93.5	1.05
4	Hydrated Lime Injection	11.4	96.4	1.08
5	Activated Carbon Injection	11.4	96.4	1.08
6	Coal - 25% Char	11.4	100.9	1.09
7	Coal - 25% Char	11.4	93.5	1.01
8	Coal - 25% Char	11.4	114.5	1.23
9	Coal - 25% Char	18.2	160.1	1.08
10	Coal - 25% Char	11.4	79.4	0.85
11	Coal - 12.5% Char	11.4	100.9	1.08
12	Coal - 12.5% Activated Carbon	11.4	102.0	1.09
13	Coal - 50% Char	11.4	103.2	1.08

¹ Stoichiometric ratio is actual A/F divided by stoichiometric A/F.

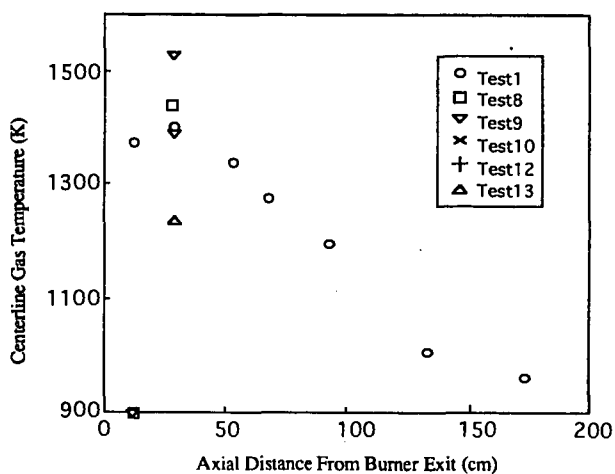


Figure 1. Gas temperature measurements for selected CPR combustion tests.

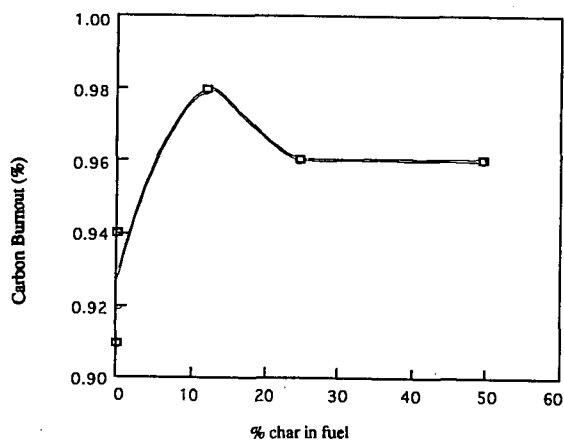


Figure 2. Effect of char concentration in the fuel on carbon burnout.

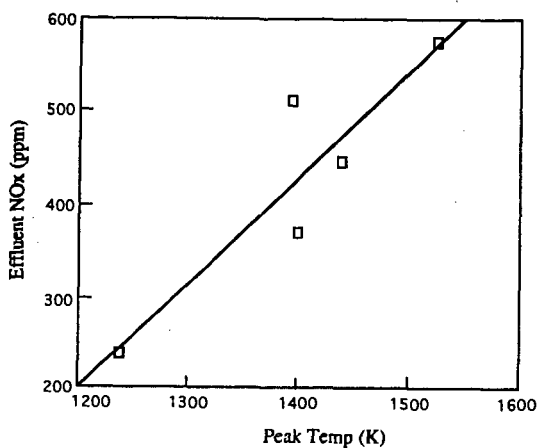


Figure 3. Relationship of peak flame temperature with measured effluent NOx concentration.

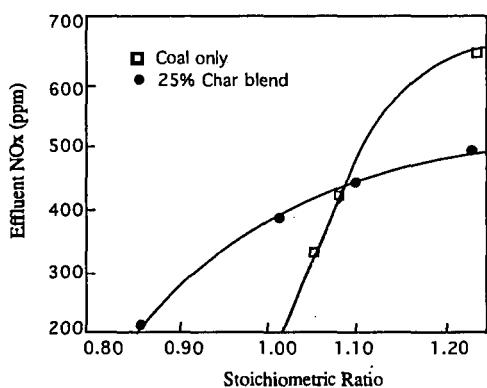


Figure 4. Effect of stoichiometric ratio on effluent NOx (Fuel feed 11.4 kg/hr).

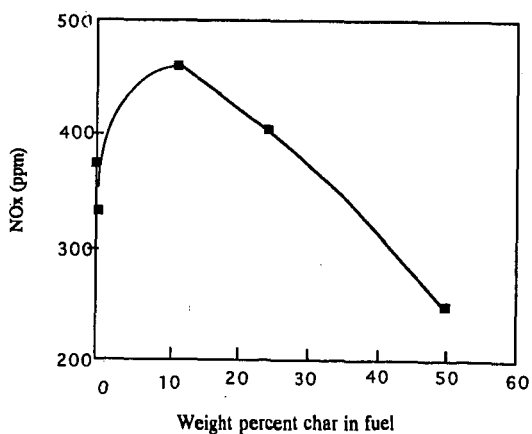


Figure 5. Effect of char concentration on effluent NOx emissions (corrected for burnout and thermal NOx; fuel feed 11.4 kg/hr, SR = 1.08).